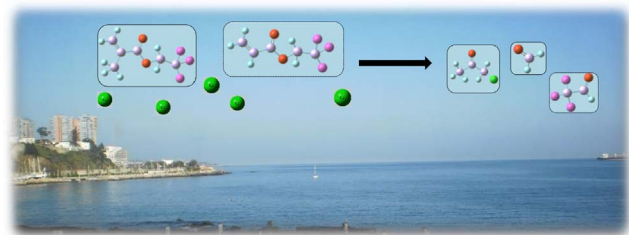# Atmospheric degradation of industrial fluorinated acrylates and methacrylates with Cl atoms at atmospheric pressure and 298 K

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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

The gas-phase reaction of Cl atom with 2,2,2-trifluoroethylacrylate (k_1), 1,1,1,3,3,3-hexafluoroisopropylacrylate (k_2), 2,2,2-trifluoroethylmethacrylate (k_3) and 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (k_4), have been investigated at 298 K and 1 atm using the relative method by gas chromatography coupled with flame ionization detection (GC-FID). The values obtained are (in cm^3 $molecule^{-1}$ s^{-1}): $k_1(Cl + CH_2=CHC(O)OCH_2CF_3) = (2.41 \pm 0.57) \times 10^{-10}$, $k_2(Cl + CH_2=CHC(O)OCH(CF_3)_2) = (1.39 \pm 0.34) \times 10^{-10}$, $k_3(Cl + CH_2=C(CH_3)C(O)OCH_2CF_3) = (2.22 \pm 0.45) \times 10^{-10}$, and $k_4(Cl + CH_2=C(CH_3)C(O)OCH(CF_3)_2 = (2.44 \pm 0.52) \times 10^{-10}$. Products identification studies were performed by solid-phase microextraction (SPME) method, with on-fiber products derivatization using *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride, coupled with gas chromatography with mass spectrometry detection (GC-MS). Chloroacetone, trifluoroacetaldehyde and formaldehyde were observed as degradation products and a general mechanism is proposed. Additionally, reactivity trends and atmospheric implications are discussed. Significant ozone photochemical potentials (POCP) and acidification potentials lead to local and or regional impact of the esters under study although is expected to a have a minor impact on global warming and climate change.

1. Introduction

Atmospheric chemistry is currently focused on a number of major environmental issues. Halogenated species, as fluorinated, has attracted a great deal of research interest with implications to gas phase interactions in the troposphere. They present an important chemistry since are widely emitted into the atmosphere from high industrial production, proc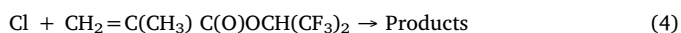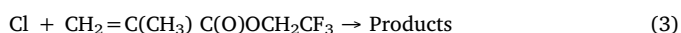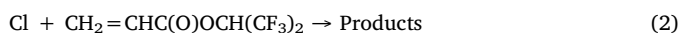essing and disposal (Takagi et al., 1997; National Research Council, 2012; Lu et al., 2013; Zhao et al., 2013; Girard et al., 2014). The large-scale production is due to its many applications, among them we can mention: chemical extraction, manufacture of polymers, precursors in cosmetic aromatic bases, cleaning agents and components of electronics, which could result in release of these compounds into the atmosphere (Barnes, 2010). According to the oxygenated functionalities in the compound, many unsaturated oxygenated volatile organic compounds (OVOCs) will be as reactive and sometimes more reactive than

their analogous alkenes, also the double bond of the molecule is very receptive to the addition of oxidants such as tropospheric OH, NO$_3$ radicals, and O$_3$ molecules. Reactions with Cl atoms play an important role in atmospheric chemistry since volatile organic compounds (VOCs) react with them generally in an order of magnitude faster than OH reactions.

It has been observed that on costal urban areas, for brief period of time at sunrise the Cl concentration produced by photolysis of molecular chlorine (Cl$_2$) can be 1×10^5 atoms cm^{-3} or higher in the marine boundary layer (Spicer et al., 1998; Lawler et al., 2009). Furthermore, it has been detected significant levels of photolabile nitrile chloride (ClNO$_2$) species in mid continental areas, all of this has expanded the knowledge about the atmospheric degradation of VOCs with Cl atoms chemistry (Osthoff et al., 2008; Thornton et al., 2010; Mielke et al., 2011; Philips et al., 2012). Fluorinated acrylates and methacrylates in these work contain Fluorine (F) atom and it is known that fluorine atom is the most electronegative of the elements its replacement by a hydrogen atom. The substitution of a hydrogen atom for a fluorine atom in an organic molecule modifies its thermal, chemical and biological characteristics. The bond formed by C-F atoms is very strong, but the intramolecular interactions of the fluorocarbons are weak. As a result, a unique combination of fluorocarbon properties, such as chemical, thermal and biological inertia, low solubility in water and polar and non-polar organic solvents, high density, flow ability, compressibility and high dielectric constants are obtained (Johns and Stead, 2000). The widespread use of these fluoropolymers could have a great impact on the quality of the air and consequently on the environmental ones, among them we can mention the climatic change (McCulloch, 2003). The fluorinated acrylates and methacrylates have many industrial applications, since they have, monomers used for develop a family of fluorinated compounds that contain vinyl polymers for Hi-Tech applications (Boschet et al., 2010). Furthermore, fluorine containing polymers (fluoroelastomers) have several important applications e.g. in O-rings, gaskets and in different automobile parts which requires high temperature oil resistance property (Koiry et al., 2013). Fluorinated acrylates and methacrylates are listed as a high (H) production (P) volume (V) chemicals in the OECD (Organisation for Economic Co-operation and Development) integrated HPV database (http://cs3-hq.oecd.org/scripts/hpv/index.asp). We have previously reported the rate coefficients of fluorinated acrylates and methacrylates 2,2,2-trifluoroethylacrylate, 1,1,1,3,3,3-hexafluoroisopropylacrylate, 2,2,2-trifluoroethylmethacrylate and 1,1,1,3,3,3-hexafluoroisopropylmethacrylate initiated by OH radicals at 298 K using relative method by GC-FID (Tovar and Teruel, 2014). In order to increase the knowledge of fluorinated acrylates and methacrylates, it is necessary to assess the importance of other sink of these industrial compounds as the gas-phase reaction of the of the compounds in this work together with to study the products obtained to postulate atmospheric chemical mechanisms for Cl atoms reactions. Due to the importance of Cl-initiated degradation reactions and the absence of kinetic and product data, in this work, we present for the first time rate coefficients determinations of the reactions of 2,2,2-trifluoroethylacrylate (TFEA), 1,1,1,3,3,3-hexafluoroisopropylacrylate (HFIA), 2,2,2-trifluoroethylmethacrylate (TFEM) and 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (HFIM) with Cl atoms at 298 K and 760 Torr:

$$Cl + CH_2{=}CHC(O)OCH_2CF_3 \rightarrow Products \quad (1)$$

$$Cl + CH_2{=}CHC(O)OCH(CF_3)_2 \rightarrow Products \quad (2)$$

$$Cl + CH_2{=}C(CH_3)\,C(O)OCH_2CF_3 \rightarrow Products \quad (3)$$

$$Cl + CH_2{=}C(CH_3)\,C(O)OCH(CF_3)_2 \rightarrow Products \quad (4)$$

To the best of our knowledge, the rate coefficients for the reactions of Cl atoms with the fluorinated acrylates and methacrylates have not been previously reported. Hence, the kinetic data presented are the first

determinations of the title reactions. Kinetic results are rationalized in terms of reactivity trends by comparison with others hydrogenated and fluorinated esters. In addition, product studies using the GC-MS technique under atmospheric conditions were carried out for the (1–4) reactions and the degradation pathways in the atmosphere are discussed. Chloroacetone and formaldehyde were identified as the main products of reaction of methacrylates with Cl atoms. In regard to the reaction of 2,2,2-trifluoroacrylate with Cl atoms, trifluoroacetaldeyde was identified as unique product of this reaction, whereas that, in the reaction between 1,1,1,3,3,3-hexafluoroisopropilacrylate with Cl atoms, it could not be observed any product formation in our experimental conditions.

To assess the possible atmospheric implications of the studied reactions, atmospheric lifetimes of the fluorinated acrylates and methacrylates involved were calculated taking into account the experimental rate coefficients obtained in this work. Environmental impact is discussed at local, regional and global scale by the determination of ozone photochemical potential (POCP), acidification potential and global warming potential of the unsaturated esters studied in the present work.

2. Experimental

The kinetic experiments were performed in a Teflon chamber of 80-L placed in a wooden box with the internal walls covered with aluminum foil. Organic reactants were measured from calibrated bulbs and were introduced into the chamber through a stream of nitrogen. Then, the chamber was filled to its full capacity at atmospheric pressure with nitrogen. We have used nitrogen as bath gas for the kinetics experiments and synthetic air for the products distribution analysis.

Cl atoms were generated by photolysis at 254 nm of oxalyl chloride (ClC(O)C(O)Cl):

$$ClC(O)C(O)Cl + h\nu \rightarrow 2Cl + 2CO \quad (5)$$

Before each experiment, the reactor was cleaned by filling it with a mixture of O$_2$ and N$_2$ which was photolyzed for 10 min using 6 germicidal lamps (Philips 30W) with a UV emission at 254 nm, to produce O$_3$. After this procedure, the reactor was cleaned again by repeated flushing with N$_2$ and checked before performing the experiments by gas chromatography that there were no observable impurities. Gas samples were taken from the Teflon reactor using calibrated gas syringes. The organic compounds were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID), using a Porapak Q column (Alltech, 2.3 m) held at a temperature of 160 °C for these compounds.

In the presence of Cl atom, fluorinated acrylates and methacrylates (FAM) 2,2,2-trifluoroethylacrylate, 1,1,1,3,3,3-hexafluoroisopropylacrylate, 2,2,2-trifluoroethylmethacrylate, 1,1,1,3,3,3-hexafluoroisopropylmethacrylate and the reference compounds, decay through the following reactions:

$$Cl + FAM \rightarrow Products \quad (6)$$

$$Cl + Reference \rightarrow Products \quad (7)$$

Provided that the reference compound and the reactant are lost only by reactions (6) and (7), then it can be shown that:

$$\ln\left\{\frac{[FAM]_0}{[FAM]_t}\right\} = \frac{kFAM}{k\,\mathrm{Re}f}\ln\left\{\frac{[Ref]_0}{[Ref]_t}\right\} \quad (8)$$

where, [Fluorinated acrylates or methacrylates]$_0$, [Reference]$_0$, [Fluorinated acrylates or methacrylates]$_t$ and [Reference]$_t$ are the concentrations of the fluorinated esters and references compounds at times $t = 0$ and t, k_{6FAM} and k_{7Ref} are the rate coefficients of reactions (6) and (7), respectively.

The relative rate technique relies on the assumption that these fluorinated acrylates and methacrylates and the reference organics are

removed only by reaction with the oxidant specie (Cl). To verify this assumption, mixtures of oxalyl chloride with N_2 and both organics were prepared and allowed to stand in the dark during two hours. In all cases, the reaction of the organic species with the precursor of Cl (ClC(O)C(O)Cl), in the absence of UV light, was of negligible importance over the typical time periods used in this work. It has been realized test for possible photolysis of the compounds studied, for this, reactants in nitrogen, in the absence of oxidants, were irradiated using the output of all germicidal lamps surrounding the chamber for 30 min. It was not observed any photolysis of fluorinated or references. Also, the linearity of the data points with correlation coefficients > 0.99 and the good agreement of the results obtained using different reference compounds support that secondary process are negligible.

The initial concentration used in the experiments were in the range of 180–200 ppm (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K and 760 Torr of total pressure) for fluorinated acrylates or methacrylates. The concentration of ClC(O)C(O)Cl were in the range of 160–180 ppm in around 760 Torr of N_2. A mixture of unsaturated fluorinated acrylates or methacrylates/ClC(O)C(O)Cl/air were analyzed after irradiation in order to identify the products formed in the reactions studied.

Products identification experiments were performed using GC-MS analytical technique, a Shimadzu GC-MS QP 5050 spectrometer equipped with a capillary column ZB-5MS (5% phenyl, 95% dimethylpolysiloxane) of 30 m - 0,25 mm. Gas samples were removed from the Teflon chamber using solid phase microextraction (SPME) as a preconcentration technique of the analytes. The SPME technique involves the extraction of analytes from the sample matrix using a silica fiber generally cover with an absorbent polymer, followed by desorption of analytes by the temperature on the injection port. In this study we have used the [divinylbenzene/Carboxen/polydimethylsiloxane] (DVB/CAR/PDMS) from Supelco, Bellefonte, PA, USA, indicated for this type of compounds. The exposure time was 1 min, and 2 min of desorption in the injection port. The determinations were carried out under atmospheric conditions. For the Cl atoms reactions mixture of fluorinated ester/ClC(O)C(O)Cl/air also were flushed into the Teflon bag. The photolysis time was 15 s for each experiment. In order to identify carbonyl products, the o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) derivatizing agent was used. The PFBHA reacts with carbonyl compounds forming a stable oxime. A 2 mL aqueous solution of PFBHA (25 mg/mL) was prepared in a 4 mL vial. The PFBHA was loaded on the SPME fiber during 90 s by head-space extraction. The fiber-PFBHA was exposed inside the chamber other 60 s to produce the oxime on the fiber to be transferred to the GC-MS injector. The desorption time was 2 min at 225 °C. The column employed was Zebron ZB-5MS (30 m × 0.25 mm x 0.25 μm). The temperature program was 80 °C for 5 min, 100 °C for 5 min, 200 °C for 15 min to 250 °C at a rate of 15°/min for the Cl atoms reactions with fluorinated acrylates and methacrylates.

3. Materials

The following chemicals with purities declared by the supplier were used: N_2 (AGA, 99.999%), synthetic air (Air Liquide, 99.999%), 2,2,2-trifluoroethylacrylate (Aldrich, 99%), 1,1,1,3,3,3-hexafluoroisopropylacrylate (Aldrich, 99%), 2,2,2-trifluoroethylmethacrylate (Aldrich, 99%), and 1,1,1,3,3,3-hexafluoroisopropylmethacrylate (Aldrich, 99%), vinyl propionate (Aldrich, 98%), 2-methyl-3-buten-2-ol (Aldrich, 96%), acrylonitrile (Baker, 99.5%), diethyl ether (Fluka, 99%), ethyl acrylate (Aldrich, 99%), oxalyl chloride (Aldrich, 99%), o-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine hydrochloride (Aldrich, 98%).

4. Results and discussion

Relative rate coefficients for the reactions of Cl atoms with fluorinated acrylates and methacrylates were determined. The data were fitted to a straight line by the linear least-squares procedure. The losses
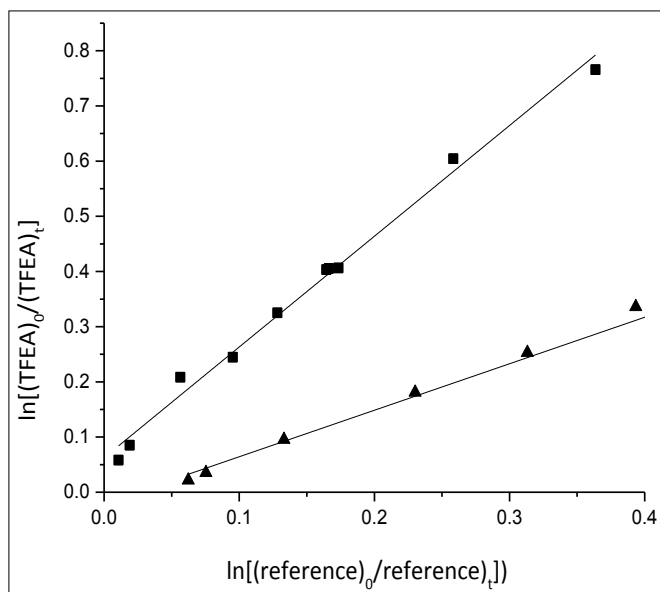

Fig. 1. Relative kinetic plot of the reaction of Cl atoms with TFEA using Acrylonitrile (■) and Ethyl acrylate (▲) as references at 298 K and 760 Torr.
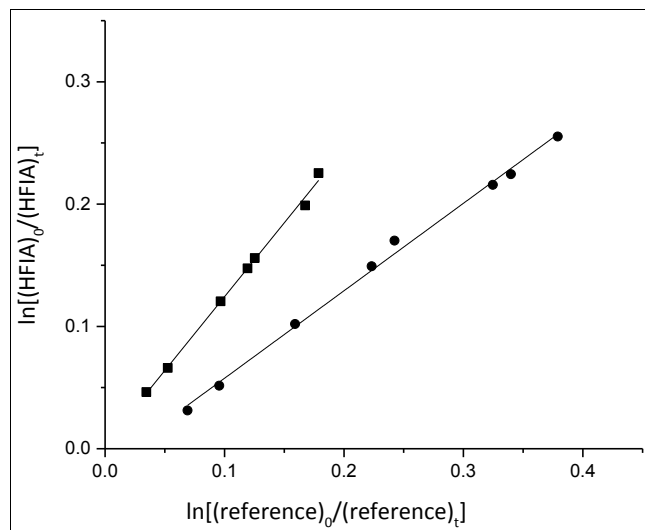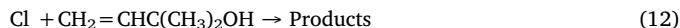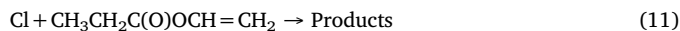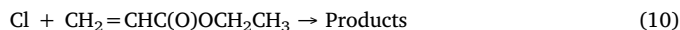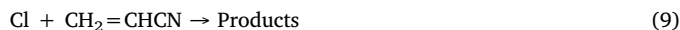

Fig. 2. Relative kinetic plot of the reaction of Cl atoms with HFIA using Acrylonitrile (■) and Vinyl Propionate (●) as references at 298 K and 760 Torr.

of TFEA, HFIA, TFEM and HFIM by Cl atoms are shown with different reference compounds in Figs. 1–4. For each reaction, four experiments were performed for the rate coefficient determination; nevertheless, only one example is displayed in Figs. 1–4.

The following compounds were used as reference reactions: acrylonitrile, ethyl acrylate, vinyl propionate, 2-methyl-3-buten-2-ol and diethyl ether to determine the rate coefficient of the reactions (1) to (4):

$$Cl + CH_2=CHCN \rightarrow Products \qquad (9)$$

$$Cl + CH_2=CHC(O)OCH_2CH_3 \rightarrow Products \qquad (10)$$

$$Cl + CH_3CH_2C(O)OCH=CH_2 \rightarrow Products \qquad (11)$$

$$Cl + CH_2=CHC(CH_3)_2OH \rightarrow Products \qquad (12)$$

$$Cl + (C_2H_5)_2O \rightarrow Products \qquad (13)$$

Where $k_9 = (1.11 \pm 0.23) \times 10^{-10}$ (Teruel et al., 2007), $k_{10} = (2.53 \pm 0.46) \times 10^{-10}$ (Teruel et al., 2009), $k_{11} = (2.06 \pm 0.36) \times 10^{-10}$ (Teruel et al., 2009), $k_{12} = (3.00 \pm 0.41) \times 10^{-10}$
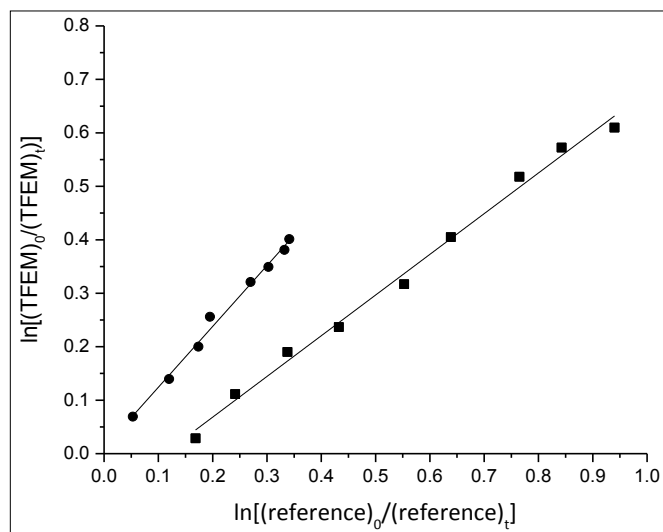
Fig. 3. Relative kinetic plot of the reaction of Cl atoms with TFEM using (■) 2-Methyl-3-buten-2-ol and Vinyl Propionate (●) as references at 298 K and 760 Torr.
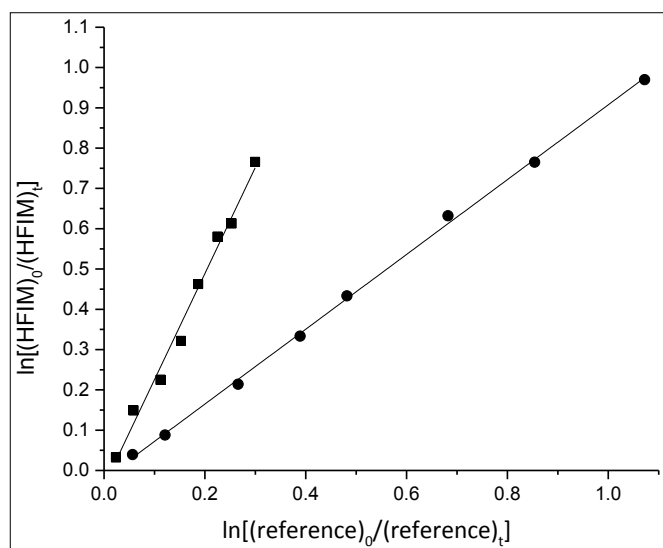

Fig. 4. Relative kinetic plot of the reaction of Cl atoms with HFIM using (■) Acrylonitrile and Diethyl ether (●) as references at 298 K and 760 Torr.

(Takahashi et al., 2010), $k_{13} = (2.54 \pm 0.18) \times 10^{-10}$ (Nelson et al., 1990). All the k values are in units of cm^3 molecule^{-1} s^{-1}.

The data on relative rate coefficients ($k_{FAM}/k_{Reference}$) and the absolute rate coefficients k_{FAM} at room temperature (298 K) are presented in Table 1. The ratios were obtained from the average values using different initial concentrations of the reactants. It is gratifying to note the agreement between the experiments conducted with different reference compounds. The rate coefficients obtained by averaging the values from different experiments were the following:

$k_{Cl + TFEA} = (2.41 \pm 0.57) \times 10^{-10} cm^3$ molecule^{-1} s^{-1}

$k_{Cl + HFIA} = (1.39 \pm 0.34) \times 10^{-10} cm^3$ molecule^{-1} s^{-1}

$k_{Cl + TFEM} = (2.22 \pm 0.45) \times 10^{-10} cm^3$ molecule^{-1} s^{-1}

$k_{Cl + HFIM} = (2.44 \pm 0.52) \times 10^{-10} cm^3$ molecule^{-1} s^{-1}

The errors quoted are twice the standard deviation arising from the least squares fit of the straight lines, to which we have considered also the corresponding error on the reference rate coefficients. To the best of our knowledge, there are no other prior reported values of the rate

Table 1
Reference compound, measured rate coefficient ratios, $k_{FAM}/k_{reference}$, and the obtained rate coefficients for the reactions of Cl atoms with TFEA, HFIA, TFEM and HFIM at 298 K in 760 Torr of nitrogen.

FAM	Reference	$k_{FAM}/k_{Reference}$	k (cm^3 molecule^{-1}s^{-1})
CH$_2$ = CHC(O) OCH$_2$CF$_3$ + Cl	Acrylonitrile	(1.95 ± 0.01)	(2.16 ± 0.24) × 10^{-10}
	Acrylonitrile	(2.19 ± 0.06)	(2.43 ± 0.57) × 10^{-10}
	Ethyl acrylate	(0.93 ± 0.01)	(2.35 ± 0.45) × 10^{-10}
	Ethyl acrylate	(1.07 ± 0.02)	(2.71 ± 0.54) × 10^{-10}
	Average		**(2.41 ± 0.57) × 10^{-10}**
CH$_2$ = CHC(O)OCH (CF$_3$)$_2$ + Cl	Acrylonitrile	(1.24 ± 0.01)	(1.38 ± 0.29) × 10^{-10}
	Acrylonitrile	(0.97 ± 0.02)	(1.08 ± 0.24) × 10^{-10}
	Vinyl Propionate	(0.73 ± 0.02)	(1.50 ± 0.30) × 10^{-10}
	Vinyl Propionate	(0.77 ± 0.03)	(1.59 ± 0.34) × 10^{-10}
	Average		**(1.39 ± 0.34) × 10^{-10}**
CH$_2$ = C(CH$_3$)C(O) OCH$_2$CF$_3$ + Cl	2-Methyl-3-buten-2-ol	(0.73 ± 0.02)	(2.19 ± 0.36) × 10^{-10}
	2-Methyl-3-buten-2-ol	(0.78 ± 0.01)	(2.34 ± 0.35) × 10^{-10}
	Vinyl Propionate	(1.14 ± 0.02)	(2.35 ± 0.45) × 10^{-10}
	Vinyl Propionate	(0.97 ± 0.02)	(2.00 ± 0.39) × 10^{-10}
	Average		**(2.22 ± 0.45) × 10^{-10}**
CH$_2$ = C(CH$_3$)C(O) OCH (CF$_3$)$_2$ + Cl	Diethyl ether	(0.98 ± 0.04)	(2.48 ± 0.28) × 10^{-10}
	Diethyl ether	(0.92 ± 0.01)	(2.33 ± 0.19) × 10^{-10}
	Acrylonitrile	(1.97 ± 0.05)	(2.18 ± 0.44) × 10^{-10}
	Acrylonitrile	(2.58 ± 0.06)	(2.78 ± 0.52) × 10^{-10}
	Average		**(2.44 ± 0.52) × 10^{-10}**

coefficients for the reactions (1) to (4) of Cl atoms with fluorinated acrylates and methacrylates. Thus, the present work is the first kinetic study of these reactions and therefore no direct comparison with the literature could be made.

However, it is interesting to compare the rate coefficients of the reactions of Cl atoms with unsaturated esters with those that have fluorine substitution in the molecule in order to rationalize the effect of substituents on the reactivity of the esters toward Cl atoms.

4.1. Reactivity trends

Table 2 shows a comparison between the rate coefficients of the reactions of OH radicals and Cl atoms with a series of unsaturated esters and the kinetic data obtained in this study for fluorinated acrylates and methacrylates. With regard to OH radicals reactions, it is possible to observe generally that when H atoms are replaced by F atoms the rate coefficient values decrease: $k_{CH2 = CHC(O)OCH2CH3 + OH} = (1.70 \pm 0.40) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} > $k_{CH2 = CHC(O)OCH2CF3 + OH} = (1.25 \pm 0.13) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{CH2 = C(CH3)C(O)OCH2CH3 + OH} = (4.58 \pm 0.59) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} > $k_{CH2 = C(CH3)C(O)OCH2CF3 + OH} = (2.54 \pm 0.12) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $k_{CH2 = C(CH3)C(O)OCH(CH3)2 + OH} = (2.28 \pm 0.25) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} > $k_{CH2 = C(CH3)C(O)OCH (CF3)2 + OH} = (1.41 \pm 0.11) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This difference can be attributed to the negative inductive effect of the F atoms substituents (Hurley et al., 2007), therefore the –CF$_3$ group reduces the partial negative charge, then electrophilic addition of OH radicals to the double bond in fluorinated acrylates and methacrylates is less favored compared to the addition to non-fluorinated esters. On the other hand, for Cl atoms reactions, the rate coefficients values of non-fluorinated esters are similar to the rate coefficients values of the fluorinated esters within experimental uncertainties. Therefore, the effect of –F atoms substituents on the reactivity of the double bond for Cl atoms is less important than the effect observed with OH addition, probably because

Table 2
Comparison of the rate coefficients values for the reaction of OH radicals with hydrogenated esters and fluorinated acrylates and methacrylates at 298 K.

VOC	k_{OH}(cm^3 molecule^{-1}s^{-1})	k_{Cl}(cm^3 molecule^{-1}s^{-1})
$CH_2=CHC(O)OCH_2CF_3$	$(1.25 \pm 0.13) \times 10^{-11a}$	$(2.41 \pm 0.57) \times 10^{-10b}$
$CH_2=CHC(O)OCH_2CH_3$	$(1.70 \pm 0.40) \times 10^{-11c}$	$(2.53 \pm 0.46) \times 10^{-10d}$
$CH_2=CHC(O)OCH(CF_3)_2$	$(1.41 \pm 0.11) \times 10^{-11a}$	$(1.39 \pm 0.34) \times 10^{-10b}$
$CH_2=CHC(O)OCH$ $(CH_3)_2$	-	-
$CH_2=C(CH_3)C(O)$ OCH_2CF_3	$(2.54 \pm 0.12) \times 10^{-11a}$	$(2.22 \pm 0.45) \times 10^{-10b}$
$CH_2=C(CH_3)C(O)$ OCH_2CH_3	$(4.58 \pm 0.59) \times 10^{-11e}$	$(2.71 \pm 0.21) \times 10^{-10f}$
$CH_2=C(CH_3)C(O)OCH$ $(CF_3)_2$	$(1.65 \pm 0.14) \times 10^{-11a}$	$(2.44 \pm 0.52) \times 10^{-10b}$
$CH_2=C(CH_3)C(O)OCH$ $(CH_3)_2$	$(2.28 \pm 0.25) \times 10^{-11g}$	$(2.50 \pm 0.78) \times 10^{-10g}$

[a] (Tovar and Teruel, 2014).
[b] This work.
[c] (Teruel et al., 2006).
[d] (Teruel et al., 2009).
[e] (Blanco et al., 2006).
[f] (Porrero et al., 2010).
[g] (Blanco et al., 2009).

the reactions with Cl atoms, in general, are less selective than the reaction in organic compounds with OH radicals (Bravo et al., 2013). The rate coefficients values reported in this work for the reactions studied are in close agreement with the rate coefficients of Cl atoms with similar unsaturated esters. Rodríguez et al., have reported values (in units of cm^3 molecule^{-1} s^{-1}) for the rate coefficients of Cl + allyl trifluoroacetate and Cl + vinyl trifluoroacetate reactions of $(1.75 \pm 0.21) \times 10^{-10}$ and $(2.08 \pm 0.16) \times 10^{-10}$, respectively using a 200 L Teflon bag and GC-FID as detection system (Rodríguez et al., 2016).

4.2. Products identification study

In addition to the kinetic study, the products of the reaction of fluorinated acrylates and methacrylates studied in this work with Cl atoms were identified and the gas phase mechanisms were postulated.

For the compounds under study, Cl atoms reactions proceed mainly by initial addition of Cl to the $>C=C<$ bond and, in absence of NOx, the alkyl radicals formed react with O_2 to lead peroxy radicals. These peroxy radicals will undergo self- and cross-peroxy reactions which will result, in the formation of 1,2-chloroalkoxy radicals (Calvert et al., 2000). This behavior has also been observed in the reaction with Cl atoms with fluorinated esters (Rodríguez et al., 2016).

The 1,2-chloroalkoxy radicals can lead the formation of final products by different pathways:

Simplified exemplary reaction mechanisms for the addition reactions of Cl atoms with the fluorinated acrylates and methacrylates in the absence of NO$_x$ are shown in Figs. 5 and 6, respectively.

4.2.1. Cl reaction with TFEA and HFIA

Regarding to the reaction of Cl atoms with acrylates, possible fates of the chloroalkoxy radicals formed includes:

i) Reaction with O_2 to give $CF_3RCHOC(O)C(O)CH_2Cl$ and $HO_2^{\bullet}$ radical.

ii) Chloroalkoxy radical scission between C_2 and C_3, to give $HC(O)CH_2Cl$ and $CF_3RCHOC(O)C(O^{\bullet})$ radical.

iii) Chloroalkoxy radical scission between C_1 and C_2, to give $CF_3RCHOC(O)CHO$ and $HC^{\bullet}(Cl)H$ radical.

In the reaction of acrylates with Cl atoms we observed trifluoroacetaldehyde ($CF_3C(O)H$) as unique product of reaction of TFEA with Cl atoms. This could be explained by considering the addition of Cl

to the double bond $>C=C<$. $CF_3C(O)H$ was observed in our experimental conditions and using the derivatizing agent *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) to monitor carbonyl compounds. The presence of trifluoroacetaldehyde was observed with fragments of m/z 293 (for trifluoroacetaldoxime), 181 and 44 (see Fig. 5 channel ii). On the other hand, it could not be observed any product formation in the reaction of HFIA with Cl atoms in our experimental conditions.

4.2.2. Cl reaction with TFEM and HFIM

Regarding to the reaction of Cl with methacrylates, possible fates of the chloroalkoxy radicals formed includes:

i) -CH$_3$ elimination to give $CF_3RCHOC(O)C(O)CH_2Cl$ and $CH_3^{\bullet}$ radical.

ii) Chloroalkoxy radical scission between C_2 and C_3, to give $CF_3RCHOC(O^{\bullet})$ radical and $CH_3C(O)CH_2Cl$.

iii) Chloroalkoxy radical scission between C_1 and C_2, to give $CF_3CHROC(O)C(O)CH_3$ and $HC^{\bullet}(Cl)H$ radical.

From the analysis of the chromatogram obtained by GC-MS, it could be observed the formation of chloroacetone ($CH_3C(O)CH_2Cl$) and formaldehyde (HCOH) as products of the reaction of methacrylates with Cl atoms with the fraction m/z = 43 characteristic of the chloroacetone. Chloroacetone is produced through, C-C scission (see Fig. 6 channel ii). In our experimental conditions and using the derivatizing agent *o*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) to monitor carbonyl compounds, we have observed the presence of formaldehyde solely in the reactions of Cl atoms with the fluorinated methacrylates. In this case, the presence of formaldehyde was observed with fragments of m/z 225 (for formaldoxime), 181 and 44 (see Fig. 6 channel i). These results are in agreement a previous work performed by in situ FTIR for the reaction of methyl methacrylate with Cl atoms (Blanco et al., 2011), where it was observed chloroacetone and formaldehyde with yields of (41 ± 6) % and (23 ± 3) %, respectively. Formyl chloride and the corresponding halopyruvate, coproducts reported in the study of nonfluorinated methacrylates, have not been observed in the present experiments.

5. Atmospheric implications

Tropospheric lifetimes, τ_x, of the fluorinated acrylates and methacrylates studied in this work were calculated through the expression: $\tau_x = 1/k_x[X]$ with X = Cl. Table 3 lists the atmospheric lifetimes with respect to the reaction with Cl atoms and OH radicals obtained in our previous work (Tovar and Teruel, 2014) for comparative purposes. In the case of Cl reactions, these calculations were performed, considering a global average chlorine concentration of 1×10^4 atoms cm^{-3} (Wingenter et al., 1996). We can observe that the reactions of the fluorinated acrylates and methacrylates with Cl atoms are between 5 and 8 days, this will probably have important impact in coastal areas (Thornton et al., 2010). Regarding to reactions with OH radicals, the atmospheric lifetimes are between 5 and 11 h. Furthermore, the atmospheric lifetimes with O$_3$ molecules have been calculated using the 'Environmental Protection Agency' rate constant calculation software, AOPWINv1.91 (US Environmental Protection Agency, 2000) being obtained an atmospheric lifetime between 1 and 7 days. Unfortunately, no kinetic data are available for the reaction of these compounds with NO$_3$ radicals. The short lifetimes calculated for these compounds indicate that they could degraded close to the emission source areas, causing a local impact potentially leading photo-oxidants in the atmosphere, responsible for the formation of photochemical smog. It is possible to observe that the main tropospheric degradation pathway for the compounds studied is the reaction with OH radical. Although, in marine and certain polluted continental areas where the Cl atoms concentration can reach levels of 1×10^5 or more, Cl-atom initiated
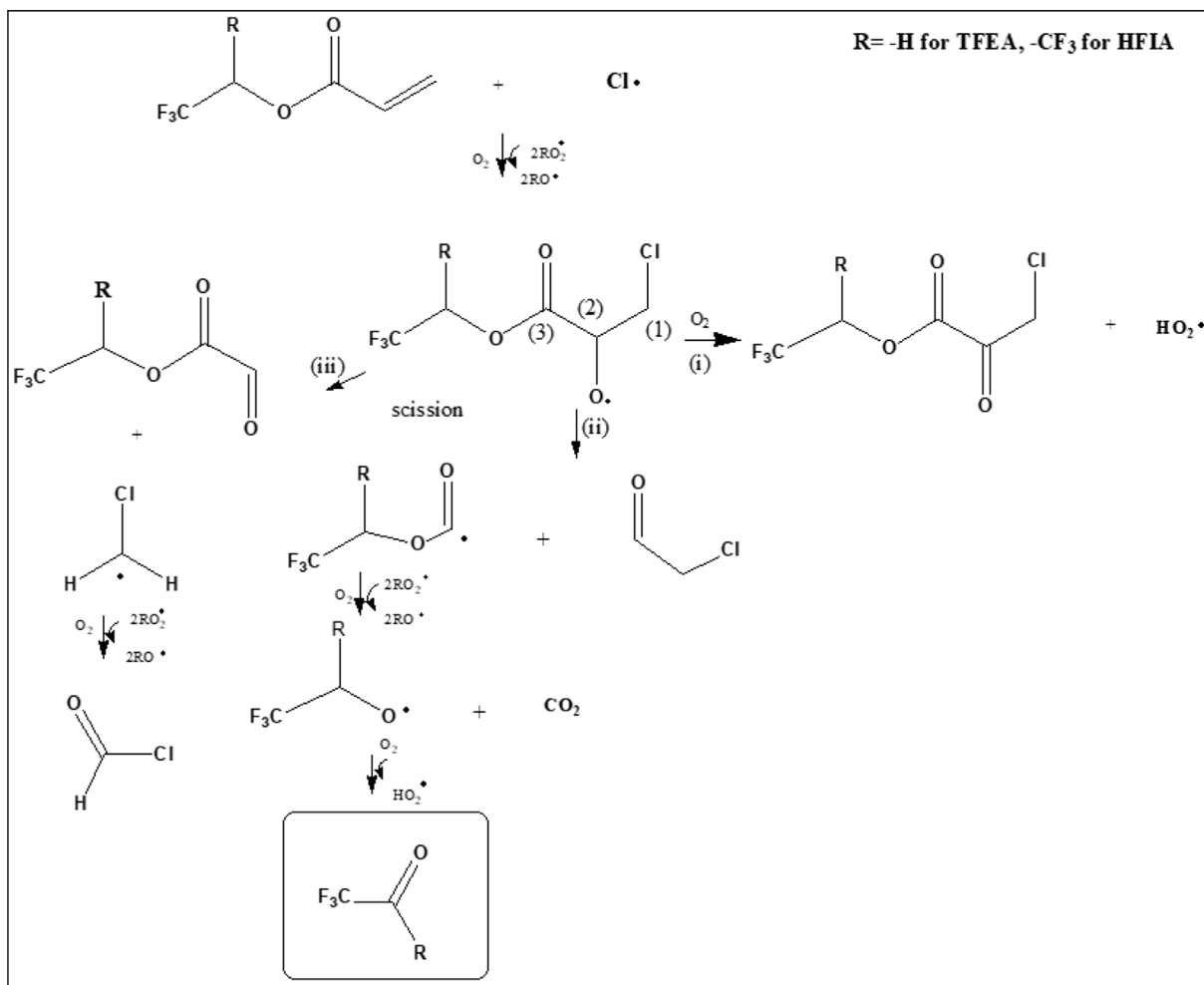
Fig. 5. Simplified mechanism for the Cl atom initiated oxidation of TFEA and HFIA via addition of Cl the double bond. The identified products are shown in filled line in the reaction between TFEA and Cl atoms.

reactions could compete with the OH reaction (Singh et al., 1996; Riedel et al., 2013). Halogenated products of these reactions studied, such as halogenated glyoxylates and pyruvates, could then react with the OH radical or Cl atoms to generate fluorinated aldehydes that could contribute to the formation of ozone and secondary organic aerosols (SOA) (Ofner et al., 2013; Zhang et al., 2017). The interactions with SOA occur in the gas phase and in the particle phase, it is known that halogens are involved in the ageing process of organic aerosols (Kroll et al., 2011). In our experimental results, chloroacetone has been identified as reaction product of TFEM and HFIM with Cl, although the main oxidant of this compound in the atmosphere is the OH radical, it is known that its reaction with Cl atoms can generate compounds as HCl and HCOCl (Carr et al., 2003). On the other hand, fluorinated formaldehyde formed in atmospheric degradation of VOCs is one the most reactive and important species in tropospheric photochemistry and ozone formation (Graedel et al., 1978). It has been observed that atmospheric lifetimes are rather short, therefore, it is expected that it will contribute significantly to the formation of ozone and other photooxidants in the atmosphere near their emission source. For this reason, the ozone photochemical potential (POCP) could be used as a modeling method to estimate the potential of ozone creation of VOCs relative to that of ethene which is given the value 100 (Derwent et al., 2007; Jenkin, 1998). This estimated method gives values of POCP for TFEA, HFIA, TFEM and HFIM around, 36, 28, 90, and 42 respectively. It can be observed that, in relation to ethene as reference compound, the TFEM could contribute significantly to the formation of tropospheric ozone. Formaldehyde (HCHO) is observed in the atmospheric

degradation of fluorinated methacrylates, with a ε^{POCP} of 119 (Derwent et al., 2007). It is known that, this small aldehyde is one of the most reactive and most important species in tropospheric photochemistry and ozone formation (Calvert et al., 2011). In addition, it is necessary to mention that Cl-initiated oxidation could be of equal importance to OH radicals, mainly in regions with high emissions, such as coastal and marine areas. In such cases, the chemistry of Cl should also be considered, and this may lead to an increase of ε^{POCP} values.

Moreover, it is important to mention that one of the environmental problems today is that of acid rain (Rengel, 2003). Although H_2SO_4, HNO_3 and HCl are the most relevant acid species in the atmosphere, it is important to note that the tropospheric oxidation of VOCs containing Cl, F, N or S in their chemical structures could contribute significantly to atmospheric acidification (de Leeuw, 1993). In accordance with the above an Acidification Potential "AP" can be defined as the number of acid equivalent potentials (H^+) per unit mass of a given compound X with respect to the number of H^+ per unit mass of the reference compound, with SO_2 being the proposed gas reference. The number of acid equivalent potentials in molecule X can be obtained by the number of Cl, F, N atoms and 2 times the number of S atoms present in the structure. Thus, the AP for X related to SO_2 is given by (de Leeuw, 1993):

$$AP\ FAM = \frac{MSO2}{MFAM} \times (nCl+nF + nN + 2.nS) \times \frac{1}{2} \quad (14)$$

Where M_{SO2} and M_{FAM} are the molecular weights of the reference compound (sulfur dioxide) and the compound in study respectively, x is
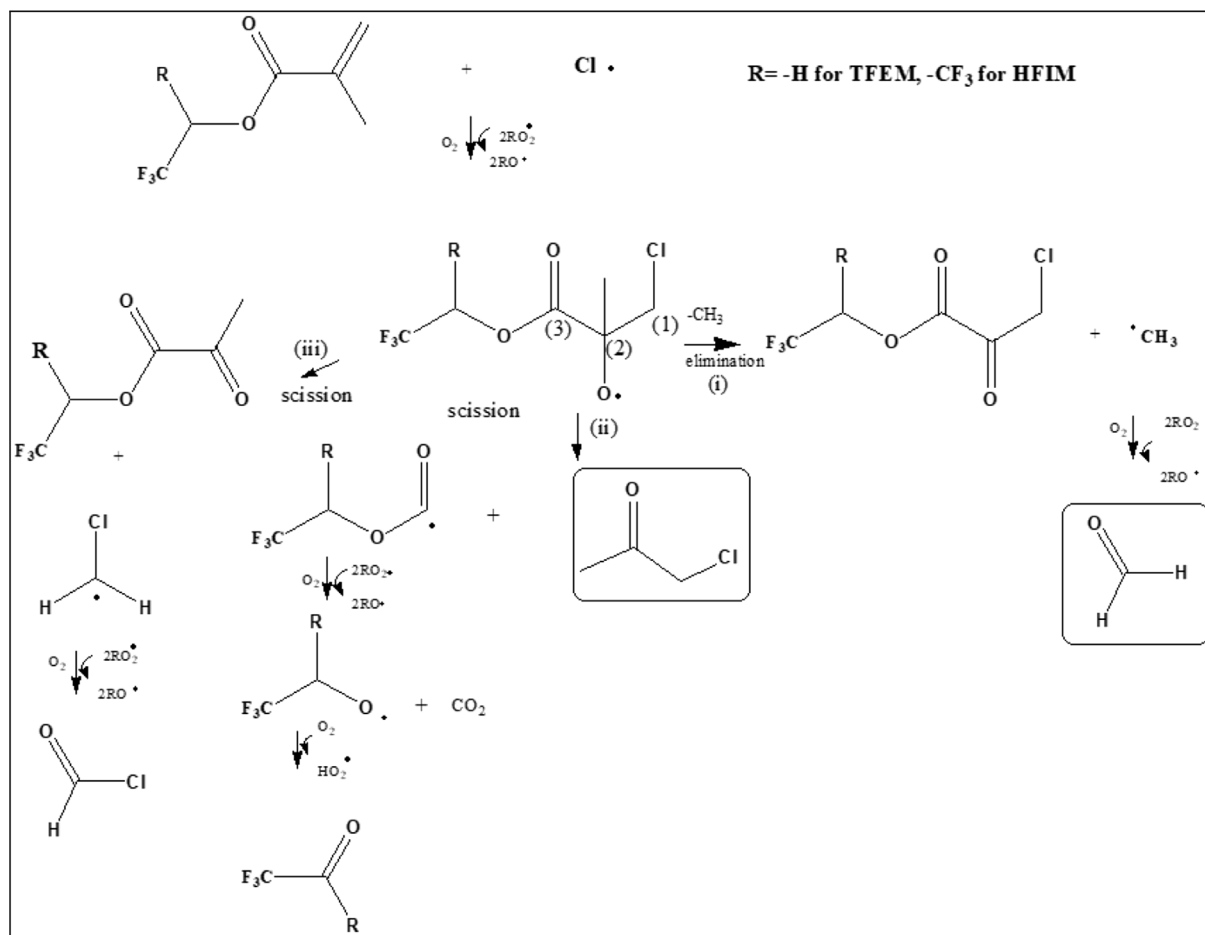
Fig. 6. Simplified mechanism for the Cl atom initiated oxidation of TFEM and HFIM via addition of to the terminal carbon of the double bond. The identified products are shown in filled line, which were observed in both reactions studied.

Table 3
Estimated tropospheric lifetimes of the fluorinated acrylates and methacrylates studied in this work with different troposphere oxidants.

FAM	τ_{OH}[a]	τ_{Cl}[b]	τ_{O3}[c]
TFEA	11 h	5 days	7 days
HFIA	10 h	8 days	7 days
TFEM	5 h	5 days	1 days
HFIM	8 h	5 days	1 days

[a] (Tovar and Teruel, 2014).
[b] This work.
[c] (US Environmental Protection Agency, 2000).

Table 4
Potential for acidification of the fluorinated acrylates and methacrylates studied and SO$_2$ as reference.

FAM	Molecular Weights	n_{total}	AP
$CH_2=CHC(O)OCH_2CF_3$	154	3	0.62
$CH_2=CHC(O)OCH(CF_3)_2$	222	6	0.86
$CH_2=C(CH_3)C(O)OCH_2CF_3$	168	3	0.57
$CH_2=C(CH_3)C(O)OCH(CF_3)_2$	236	6	0.81
SO_2	64		1

Cl, F, N and S, and n_x number of atoms of Cl, F, N and S present in the fluorinated acrylates or methacrylates structure. Analysis of potential acidification indicated in Table 4, show that the capacity of acidifying of the FAM are close to the SO$_2$ (between 0.57 and 0.81). This indicates that these compounds and their atmospheric degradation products could be involved in harmful "acid rain" events that are recorded in polluted atmospheres, if they are removed from the air by wet deposition processes.

In conclusion, the compounds studied have shorts atmospheric lifetimes and it is known that, homologous fluorinated esters which have been studied recently have short lifetime and low GWP, so they are expected to have a minor impact on global warming and climate change (Rodríguez et al., 2016). In addition, ε^{POCP} is relatively low, so compounds are expected to have no significant local effects on ozone formation, except in areas with increased levels of Cl atoms where their chemistry could increase local ozone formation. In relation to the products, it is expected that halogenated carboxylic compounds generated by the oxidation of fluorinated acrylates and methacrylates could removed by heterogeneous processes, contributing to the acidification of precipitation, producing harmful effects in both humans and biota.

Acknowledgements

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